



Short communication

Anion conducting poly(vinyl alcohol)/poly(diallyldimethylammonium chloride) membranes with high durable alkaline stability for polymer electrolyte membrane fuel cells

Jinli Qiao ^{a,*}, Jing Zhang ^a, Jiujun Zhang ^b^aCollege of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, PR China^bNRC Energy, Mining & Environment, National Research Council of Canada, 4250 Wesbrook Mall, Vancouver, BC V6T 1W5, Canada

HIGHLIGHTS

- Anion conducting PVA/PDDA-OH⁻ membranes are prepared.
- The membrane exhibits high OH⁻ conductivity of 0.025 S cm⁻¹ at 25 °C.
- The membrane shows a strong alkaline stability in 8 M KOH at 80 °C for 360 h.
- A H₂/O₂ fuel cell power density of 35.1 mW cm⁻² is reached at 25 °C.

ARTICLE INFO

Article history:

Received 19 December 2012

Received in revised form

14 February 2013

Accepted 20 February 2013

Available online 28 February 2013

Keywords:

Alkaline anion-exchange membrane

Cross-linking

Hydroxide conductivity

Alkaline stability

Membrane electrode assembly

ABSTRACT

Novel and highly durable alkaline anion-exchange membranes, PVA/PDDA-OH⁻, are synthesized using a combined thermal and chemical cross-linking method. In the synthesis, poly(vinyl alcohol) (PVA) is used as polymer matrix and poly(diallyldimethylammonium chloride) (PDDA) as anion charge carriers. The resulting membrane exhibits a high hydroxide conductivity of 0.025 S cm⁻¹ at a polymer composition PVA/PDDA being 1:0.5 by mass. A promising H₂/O₂ fuel cell peak power density of 32.7 mW cm⁻² is reached for MEA fabricated with this PVA/PDDA-OH⁻ at 25 °C. The membrane also shows a strong alkaline stability in 8 M KOH at 80 °C for 360 h. This is considered a new record for the fully cation-free hydrocarbon membranes for the use in alkaline fuel cell, seeing that PVA/PDDA-OH⁻ is made simply of aliphatic skeletons.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Alkaline polymer electrolyte membrane (PEM) fuel cells, employing alkaline anion (OH⁻)-exchange membranes (AAEMs) offer an attractive option as power sources for stationary and portable applications due to their faster electrode kinetics, lower fuel crossover, reduced CO poisoning, and use of non-precious metal catalysts [1,2]. However, since the mobility of OH⁻ is only 1/4 of that of the H⁺ transportation (membranes that conduct H⁺ cations), the membranes that can have high OH⁻ conductivity are highly desired for obtaining a higher power density. In cases where much effort has been undertaken for the above purpose [3–7], the

problem of low membrane stability, particularly alkaline stability, has also identified as one of the major barriers that affects their application in alkaline fuel cells [8–13]. However, little progress is achieved because of trade-off relations between these parameters [3–6,9,11].

Regarding the alkaline stability, AAEMs containing quaternary ammonium groups are likely to decompose in concentrated alkali solutions, especially at elevated temperatures (above 60 °C) via by either an E2 Hofmann elimination or by an SN2 substitution reaction [3–7,14–16]. In our recent work, we have been pursuing the design and the development of new families of cost-effective, readily prepared OH⁻ conducting membranes. Our approach is based on chemically cross-linked PVA polymer networks by incorporating the water-soluble quaternized copolymer as anion charge carriers. Incorporation of the above concepts has demonstrated a feasibility in preparing membranes with high hydrolytic

* Corresponding author. Tel.: +86 21 67792379; fax: +86 21 67792159.

E-mail addresses: qiaojinli@hotmail.com, qiaojl@dhu.edu.cn (J. Qiao).

(dimensional) stability and the alkaline stability with reasonable OH^- conductivity [17,18].

This communication reports promising initial performances of a new type of alkaline anion-exchange membranes by incorporating poly(diallyldimethylammonium chloride) (PDDA) as anion charge carriers. Because the PDDA contains cyclic quaternary ammonium structure, it is expected to contribute the membrane's high chemical stability along with the high dense of cross-linkages of PVA [13,17]. These PVA/PDDA-based AAEMs (abbreviated PVA/PDDA– OH^-) perform quite high OH^- conductivity, alkaline stability and power density which are much superior to our previously investigated. All of these favor properties suggest that the PVA/PDDA– OH^- membranes could be new prospects for the use in alkaline PEM fuel cells.

2. Experimental

The PVA/PDDA– OH^- membranes were formed by a solution-cast method [17]. Typically, a stock PVA (99% hydrolyzed, average $M_w = 86,000\text{--}89,000 \text{ g mol}^{-1}$, Aldrich) aqueous solution was first prepared by dissolving PVA (50 g) in distilled water (500 ml) at 90 °C with stirring. Appropriate amounts of PDDA (20% water solution, $M_w = 400,000\text{--}500,000$, Aldrich) were then mixed with the above PVA under mechanical agitation, in a controlled PVA/PDDA mass ratio of 1:0.125, 1:0.25, 1:0.5, 1:0.75 and 1:1, respectively. The resulting solutions were poured into plastic petri dishes, and water was evaporated under ambient conditions. When visually dry, the membrane was peeled from the plastic substrate with a thickness of about 60–80 μm .

The membranes were treated by both thermal and chemical cross-linking methods. The thermal cross-linking refers to the membranes which were annealed at different temperatures (from 110 to 150 °C) for an hour to induce physical cross-linking between PVA chains [19]. Then samples of square pieces of polymer membranes ($1 \times 1.5 \text{ cm}$) were soaked in reaction solution consisting of

10 wt.% glutaraldehyde (GA), 0.2 wt.% hydrochloric acid in acetone for further chemical cross-linking. Due to the reaction catalyzed by H^+ , the cross-linking and acetal took place between the PVA hydroxyl and the GA aldehyde groups in the membrane [17,18]. Standing and flat membranes were obtained with a thickness about 70–90 μm . The membranes were rendered conducting by immersion of PVA/PDDA in the 2 M KOH solution and equilibrated for 24 h to convert it from Cl^- into OH^- form. The OH^- exchanged membrane was washed with D.I. water until pH 7 was reached.

For fuel cell testing, the MEA was prepared by hot-pressing the PVA/PDDA– OH^- membrane with the catalyst loaded carbon paper (Toray TGP-H-090) at a pressure of 6 MPa at 50 °C for 6 min. The catalyst loading on both the anode and cathode electrodes were 0.5 mg (Pt) cm^{-2} (40%Pt/C, Johnson–Matthey). The catalyst ink was made from a solution of 5 wt.% Nafion (Aldrich). The MEA were evaluated in a single fuel cell with an active area of 4 cm^2 in H_2/O_2 gas using an electronic load. Pure hydrogen and oxygen were supplied to enter the anode and cathode channels at a flow rate of 100 and 70 ml min^{-1} , respectively, through a humidifier maintained at 25 °C under ambient pressure. Polarization curves were obtained using a fuel cell evaluation system (GE/FC1-100).

3. Results and discussion

Fig. 1(a) shows the inner structure of cross-linked PVA/PDDA composites, and **Fig. 1(b)** shows the membrane picture of PVA/PDDA– OH^- . In this work, in order to explore the most suitable thermal and chemical cross-linking methods, the ionic conductivity (σ_{Cl}^-) and water uptake (WU) of PVA/PDDA membranes were measured without KOH immersing. At this situation, the conductivity of the membrane is due to Cl^- , which is lower than the OH^- conductivity. As shown in **Fig. 1(c)**, the WU and σ_{Cl}^- values both decreases with increasing chemical cross-linking time while the thermal cross-linking was kept at 130 °C for 1 h. The decrease in WU is probably due to the increased cross-linking density of the

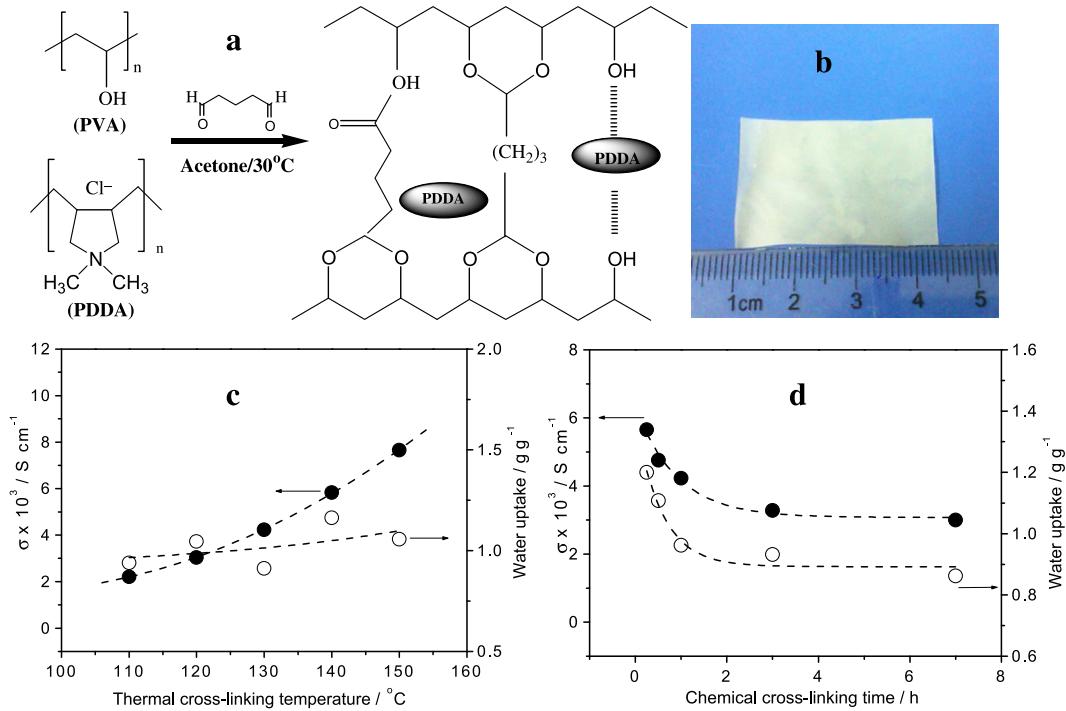


Fig. 1. (a) Chemical structure of cross-linked PVA/PDDA composite; (b) membrane picture of PVA/PDDA– OH^- ; (c) σ_{Cl}^- and WU of PVA/PDDA as a function of chemical cross-linking time (the thermal cross-linking temperature was kept at 130 °C); (d) σ_{Cl}^- and WU of PVA/PDDA as a function of thermal cross-linking temperature (the chemical cross-linking time was kept at 1 h). Polymer composition PVA/PDDA = 1:0.5 by mass.

membranes. This could make the polymer structure more rigid and compact, leading to a decrease in σ_{Cl}^- value due to the decreased free volume capable of containing water molecules. With further cross-linking time, both WU and σ_{Cl}^- tends to level-off, indicating the completion of cross-linking reaction in the membrane. In Fig. 1(c), the changes in σ_{Cl}^- and WU with thermal cross-linking temperature are shown, in which the chemical cross-linking time was kept at 1 h. As can be seen in Fig. 1(d), increasing thermal cross-linking temperature can result in an increase in σ_{Cl}^- value. The WU of the membranes, on the other hand, has no obvious changes with thermal cross-linking temperature and is around 1.0 g g^{-1} dry membrane. Obviously, the water uptake of the membranes is suppressed due to a further cross-linking reaction of PVA according to $-\text{C}_2\text{H}_3-\text{O}-\text{C}_2\text{H}_3\text{OH}-$ [19].

Fig. 2(a) shows the OH^- conductivity (σ_{OH}^-) and WU of PVA/PDDA- OH^- membranes after exchanging with 2 M KOH, as a function of PDDA content, where the PVA/PDDA mass ratio is ranged from 1:0.125 to 1:1. In all cases, PVA/PDDA- OH^- shows a much higher OH^- conductivity than the cases for our previously reported [17,18] including cross-linked quaternized PVA ($3-7 \times 10^{-3} \text{ S cm}^{-1}$) [20]. The maximum σ_{OH}^- value measured at 25°C with AC impedance spectroscopy reaches as high as 0.025 S cm^{-1} at a PVA/PDDA polymer composition of 1:0.5 by mass. In comparison with the relative OH^- conductivities of these membranes, two parameters are of particular importance, the concentration C_{OH^-} and charge carrier mobility, u_{OH^-} . It is found that PVA/PDDA- OH^- membranes showed both high charge curries and mobility. This could be demonstrated by the ion-exchange capacity (IEC) of $0.85 \text{ mequiv g}^{-1}$ with WU of around 0.96 g g^{-1} for PVA/PDDA- OH^- membranes, which is a much higher IEC and lower WU than other quaternized copolymer incorporated PVA but with a mass ratio of 1:1 [17,18]. From this interesting result we can foresee that PVA/PDDA- OH^- membranes would be a promising

candidate for AAEM fuel cells if we could find some new way to further suppress its water swelling behavior.

Alkaline stability was tracked by immersing PVA/PDDA- OH^- membrane (1:0.5 by mass) into 8 M KOH solution at 80°C . It was then washed with D.I. water for several times to remove free KOH on the membrane surface, and then the OH^- conductivity of the membrane was measured at room temperature. The resultant OH^- conductivities were recorded as a function of immersion time. As shown in Fig. 2(b), the PVA/PDDA- OH^- membrane shows an increase in OH^- conductivity during the initial 24 h, which might be due to the fact that more KOH was taken into the polymer matrix. A striking feature of the initial long-term test is that no appreciable decay of the OH^- conductivity could be observed even after 360 h of immersion and, so was the water uptake. The excellent alkaline stability of PVA/PDDA- OH^- membranes may be induced from the formation of high dense cross-linkages in the membrane and its stability by a special inner structure (five-membered heterocyclic ring), thus the β -hydrogen elimination is prohibited effectively [13]. All of this indicates that the PVA/PDDA- OH^- membranes maintain their functional group chemistries under strongly alkali conditions, and are quite stable at high temperature even when treated with a KOH concentration up to 8 M.

Fuel cell performance using PVA/PDDA- OH^- membrane (1:0.5 by mass) fabricated MEA in H_2/O_2 mode was measured (Fig. 2(c)), and the result was given in Fig. 2(d). The alkaline fuel cell exhibits an open circuit voltage (OCV) of 0.81 V and, a peak power density of 32.7 mW cm^{-2} at a current density of 72.9 mA cm^{-2} . Besides the AAEM's properties, the cell behavior can also be affected by many other factors such as catalyst loading and the MEA fabrication procedures. It can be seen that the PVA/PDDA- OH^- membrane has a quite high conductivity, alkaline stability and promising power density in comparison with other H_2/O_2 fuel cell behavior of alkaline exchange membranes (Table 1). It should be mentioned that

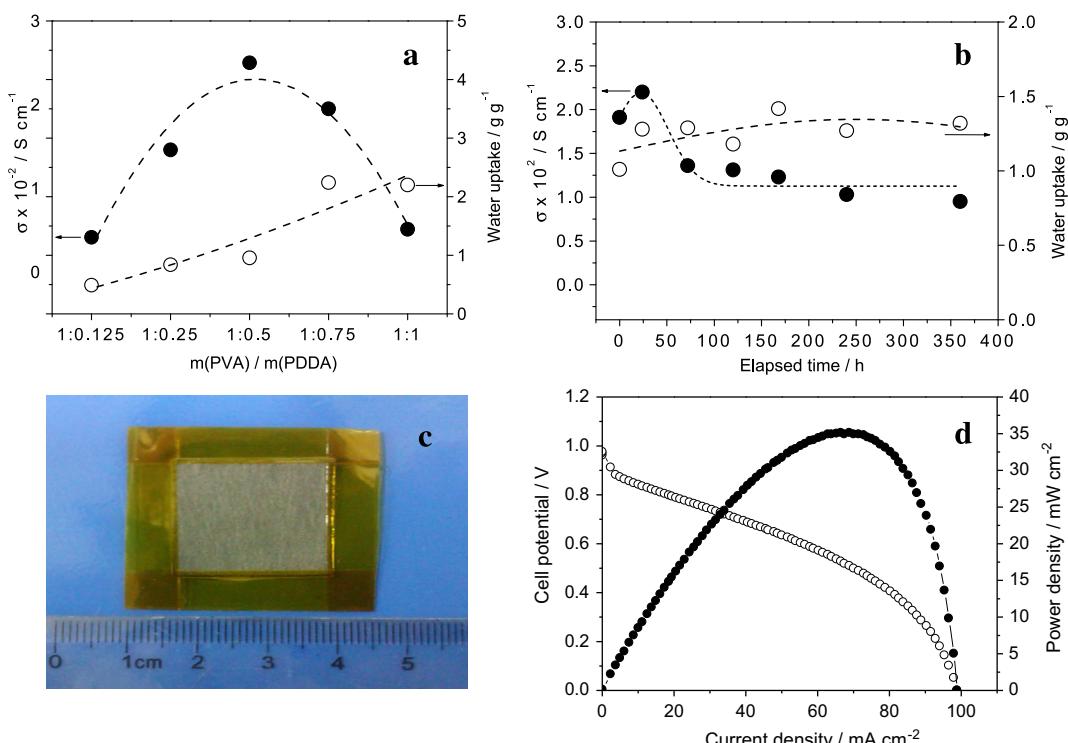


Fig. 2. (a) σ_{OH}^- and WU of PVA/PDDA- OH^- membrane as a function of PDDA content; (b) time courses of σ_{OH}^- and WU of PVA/PDDA- OH^- membrane after conditioning in 8 M KOH at 80°C , followed by complete removal of free KOH prior to testing; (c) PVA/PDDA- OH^- membrane fabricated MEA; (d) fuel cell performance of at 25°C . The catalyst loading is $0.5 \text{ mg (Pt) cm}^{-2}$ both on the anode and the cathode. Polymer composition: PVA/PDDA = 1:0.5 by mass.

Table 1Comparison of the PVA/PDDA-OH⁻ membrane and other selected alkaline anion-exchange membranes.

AAEMs	OH ⁻ conductivity (S cm ⁻¹)	Alkaline stability	Catalyst loading (mg (Pt) cm ⁻²)	Power density (mW cm ⁻²)	Cell temperature (°C)	References
GPPO	0.071	25 °C/1 M KOH/192 h	0.4	16	50	[9]
QAPSF	—	50 °C/1 M KOH/70 h	1.0	4.1	r.m.	[11]
Im-AAEM	0.032	60 °C/2 M NaOH/200 h	0.4	30	50	[5]
QPBLs	0.056/80 °C	60 °C/6 M KOH/168 h	0.5	3.1	r.m.	[7]
γ-Grafted ETFE	0.039	60 °C/10 M KOH/120 h	2	48	40	[8]
AQPVH	0.01	60 °C/1–3 M KOH/120 h	—	—	—	[6]
PEI	2.28–3.51 × 10 ⁻³	80 °C/1 M KOH	—	—	—	[3]
PVA/PDDA	0.025	80 °C/8 M KOH/360 h	0.5	32.7	r.m.	This work

most recently, with the mutual radiation grafting technique, two good candidates were reported for H₂/O₂ fuel cell using TMA functionalised (LDPE-co-VBC) [21] and poly (ETFE-g-VBC) membrane [10] by introducing nonfluorinated or partially fluorinated groups. Their cell performance reached 823 mW cm⁻² at 60 °C and 648 mW cm⁻² at 20 °C at the voltage of 0.5 V. However, high cost and complexity for membrane synthesis should be the considerable factors. To the best of our knowledge, such excellent electrochemical performance in the AAEM fuel cell has rarely been observed for PVA-based cation-free hydrocarbon membranes. Considering that PVA/PDDA-OH⁻ membranes are all hydrocarbon chains, which is very different from the fluoropolymer anion exchange membranes or other hydrocarbon membranes with aromatic skeletons, therefore, this may afford the PVA/PDDA-OH⁻ membranes a unique position compared to most of the proposed membranes for AAEM fuel cell applications.

4. Conclusions

PVA/PDDA-OH⁻ alkaline anion-exchange membranes were prepared by a combined thermal and chemical cross-linking method and successfully applied in AAEM fuel cell. The resulting membrane exhibited high OH⁻ conductivity of 0.025 S cm⁻¹ at 25 °C, which enabled a high power density of 32.7 mW cm⁻² at room temperature in a real H₂/O₂ fuel cell. The membranes exhibited a high alkaline stability in 8 M KOH at 80 °C for 360 h due to effectively suppressed β-hydrogen elimination. The refinement of the preparation conditions for both the membrane and MEA are under way to further enhance both the longevity and power performances of the use in alkaline fuel cells.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21173039), The Opening Foundation of

Zhejing Provincial Top Key Discipline and The State Environmental Protection Engineering Center for Pollution Treatment and Control in Textile Industry of China.

References

- M.A. Abdel Rahim, R.M. Abdel Hameed, M.W. Khalil, J. Power Sources 134 (2004) 160–169.
- J. Zhou, M. Ünlü, I. Anestis-Richard, P.A. Kohl, J. Membr. Sci. 350 (2010) 286–292.
- G.G. Wang, Y.M. Weng, D. Chu, D. Xie, R.R. Chen, J. Membr. Sci. 326 (2009) 4–8.
- J. Fang, P.K. Shen, J. Membr. Sci. 285 (2006) 317–322.
- I. Ran, L. Wu, J.R. Varcoe, A.L. Ong, S.D. Poynton, T.W. Xu, J. Membr. Sci. 415 (2012) 242–249.
- Y.M. Zhang, J. Fang, Y.B. Wu, H.K. Xu, X.J. Chi, W. Li, Y.X. Yang, G. Yan, Y.Z. Zhuang, J. Colloid Interface Sci. 381 (2012) 59–66.
- Z.J. Xia, Y.N. Sen, G.P. Jiang, X.X. Guo, J.H. Fang, L.L. Liu, J.L. Qiao, J. Yin, J. Membr. Sci. 390 (2012) 152–159.
- J. Fang, Y.X. Yang, X.H. Lu, M.L. Ye, W. Li, Y.M. Zhang, Int. J. Hydrogen Energy 37 (2012) 594–602.
- X.C. Lin, L. Wu, Y.B. Liu, A.L. Ong, S.D. Poynton, J.R. Varcoe, T.W. Xu, J. Power Sources 217 (2012) 373–380.
- M. Mamlouk, J.A. Horsfall, C. Williams, K. Scott, Int. J. Hydrogen Energy 37 (2012) 11912–11920.
- J.F. Zhou, M. Ünlü, J.A. Vega, P.A. Kohl, J. Power Sources 190 (2009) 285–292.
- M.R. Hibbs, C.H. Fujimoto, C.J. Cornelius, Macromolecules 49 (2009) 8316–8321.
- B. Bauer, H. Strathmann, F. Effenberger, Desalination 79 (1990) 125–144.
- D. Stoica, L. Ogier, L. Akrou, F. Alloin, J.F. Fauvarque, Electrochim. Acta 53 (2007) 1596–1603.
- H. Herman, R.C.T. Slade, J.R. Varcoe, J. Membr. Sci. 218 (2003) 147–163.
- L. Wu, T. Xu, D. Wu, X. Zheng, J. Membr. Sci. 310 (2008) 577–585.
- J.L. Qiao, J. Fu, L.L. Liu, Y.Y. Liu, Int. J. Hydrogen Energy 37 (2012) 4580–4589.
- T.C. Zhou, J. Zhang, J.L. Qiao, L.L. Liu, G.P. Jiang, J. Zhang, Y.Y. Liu, J. Power Sources 227 (2013) 291–299.
- A. Svang-Ariyaskul, R.Y.M. Huang, P.L. Douglas, R. Pal, X. Feng, P. Chen, L. Liu, J. Membr. Sci. 280 (2006) 815–823.
- Y. Xiong, J. Fang, Q.H. Zeng, Q.L. Liu, J. Membr. Sci. 311 (2008) 319–325.
- M. Mamlouk, K. Scott, J. Power Sources 211 (2012) 140–146.